Studies on Fluorine at Low Temperatures. VI. Surface Tension of Liquid Fluorine.

By Eizo KANDA.

(Received August 12th, 1937.)

Surface tension, as well as dielectric constant, is a characteristic of a liquid and its value is necessary in the determination of the state of molecule of the liquid. As to the surface tension of liquid fluorine, Moissan[1] reported that "the rise in a capillary tube of fluorine, oxygen, alcohol, and water was 3.5, 5.0, 14, and 22 respectively". As a matter of fact, however, the surface tension of oxygen is about 13 dyne/cm. at its boiling point and neighbourhood and that of water is about 71 dyne/cm. at the ordinary temperature. Thus, Moissan's report, like his note on the melting point of fluorine, is very ambiguous. He gave no numerical value except those mentioned above.

The value of vapour pressure of oxygen shows that oxygen is quite a normal liquid. Further, the molecular weight, molecular volume, boiling point, and critical point of fluorine are very close to those of oxygen, and accordingly it may, like oxygen, be conceived to be a normal liquid. In fact, the vapour pressure of liquid fluorine shows that this element is a normal liquid governed by Hildebrand's rule. In view of this fact, the author thought it necessary to obtain an exact value of its surface tension.

I. Method and Apparatus of the Experiment. The author adopted the method in which the rise in a capillary tube is observed, and consulted the method of Onnes and Kuypers[2] for the determination of the surface tension of liquid hydrogen. The apparatus used is illustrated in Fig. 1, where B_3 is a trap containing the test liquid and a capillary tube K for measuring the capillarity. In B_3 are projections b supporting the capillary tube. The capillary rise was observed by means of a comparator having an accuracy up to 1/100 mm. At the same time the vapour pressure of the liquid was measured by a quartz pressure gauge.

The temperature at which the surface tension was determined ranged from the boiling point to the melting point of fluorine. In the experiment liquid hydrogen was not used, because the phenomenon inside the Dewar

(1) Moissan, *Compt. rend.*, **125** (1897), 502.

(2) Onnes and Kuypers, *Commun. Phys. Lab. Univ. Leiden*, No. **142** (1914).

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vessel had to be distinctly observed. The Dewar vessel A_3 contained liquid oxygen and was made air-tight with a cap C fixed to the upper. D is fitted with a pump and the liquid oxygen was vigorously vaporized. In this way, the temperature up to the triple point of oxygen (85°K) was obtained.

B_1 and B_2 are traps for refining the fluorine by fractional distillation. Liquid nitrogen was used in A_1 and A_2.

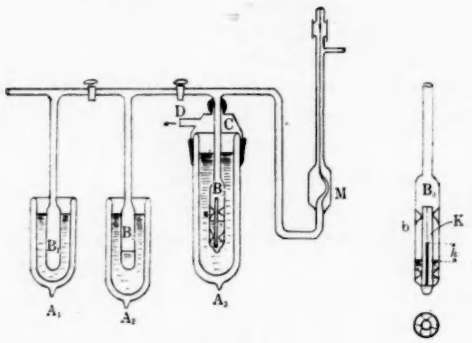

Fig. 1.

Capillary tube. As liquid fluorine is of smaller surface tension than ordinary liquids, capillary tubes having a very small inside diameter had to be used for obtaining a satisfactory rise of the liquid. Because of a small amount of rise of the liquid, however, the inside diameter of the tubes had to be uniform only for a small length. Tubes with cross-sections the most approximate to a perfect circle and with diameters about 0.16 mm. were selected from among more than 50 glass tubes by microscopic examination.

As the capillary tube would have been attacked by fluorine at ordinary temperature, fluorine was to be introduced into the trap and condensed therein after it had been cooled down to the temperature of the liquid nitrogen. The capillary tube was renewed for each series of observations.

Determination of the surface tension. The surface tension γ (dyne/cm.) is expressed by the following formula, on the assumption that the cross-section of the tube is a perfect circle and that the angle of contact is zero:

$$\gamma = \frac{1}{2} rg(\rho_l - \rho_g)h \ ,$$

where r is inside radius of the tube, g acceleration due to gravity (980), ρ_l density of the liquid (g/c.c.), ρ_g density of the coexisting vapour, and h the capillary rise (cm.). ρ_l was separately determined at various temperatures. ρ_g was calculated by using the values of vapour pressure and the temperature for each experiment.

II. Results of the Measurements with Liquid Oxygen. (Table 1).

Table 1. $r = 0.00805$ cm.

T	p(mm.)	ρ_l	ρ_g	h(cm.)	γ(dyne/cm.)
58.10	3.3	1.291	—	4.166	21.25
62.49	10.0	1.275	—	4.032	20.32
71.10	57.4	1.235	0.41×10^{-3}	3.732	18.21
76.69	142.2	1.218	0.95 ,,	3.468	16.68
81.40	274.6	1.182	1.73 ,,	3.237	15.54
89.50	711.7	1.150	4.14 ,,	2.996	13.55

These values, as compared with Baly and Donnan's[3] three values, are given in Fig. 2.

Eötvös's constant calculated from the above data was $K = 1.92$ ($T_k = 155°$), and this fact shows that oxygen is a normal liquid.

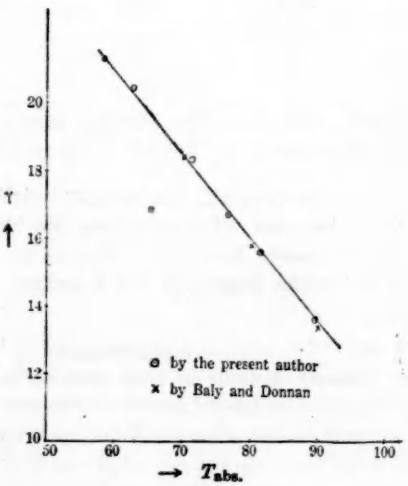

Fig. 2.

III. Surface Tension of Fluorine. Examples of measurements are given in Table 2 and values obtained with another capillary tube in Table 3.

The values of γ are graphically shown in Fig. 3. $K = 1.78$ was obtained for $\gamma v^{2/3} = K(T_k - T)$, a fact which practically conforms with Eötvös's law. Thus, liquid fluorine may also be regarded as a normal

(3) Baly and Donnan, *J. Chem. Soc.*, **81** (1902), 907.

Table 2. $r = 0.00805$ cm.

T	p	ρ_l	ρ_g	h(cm.)	γ
57.10	—	1.205	—	3.068	14.61
59.95	—	1.195	—	3.002	14.16
64.20	28.22	1.181	0.27×10^{-3}	2.884	31.46
72.11	129.90	1.155	1.10 ,,	2.654	12.10
76.30	247.50	1.140	2.02 ,,	2.536	11.40
84.91	733.50	1.112	5.76 ,,	2.254	9.85

Table 3.

T	γ
61.41	13.85
65.30	13.17
71.00	12.20
81.50	10.41

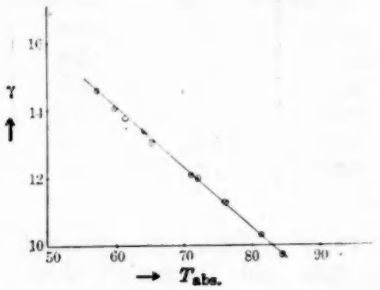

Fig. 3.

liquid. Further, the surface tension of fluorine is lower than that of liquid oxygen, but not so much as Moissan reported.

In conclusion, the author wishes to express his cordial thanks to Prof. Aoyama who gave him the kind guidance through this work. He also expresses his hearty thanks to the Japan Society for the Promotion of Scientific Research for a grant.

Cryogenic Section,
Research Institute for Iron, Steel and Other Metals,
Tohoku Imperial University.

Studies on Fluorine at Low Temperatures. VII. Determination of Dielectric Constants of Condensed Gases.

By Eizo KANDA.

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The author set about determining the dielectric constants of condensed gases as a means of studying the state of their molecules. This paper deals with the determination of the dielectric constants of liquid oxygen, fluorine, chlorine, and hydrogen chloride.

I. Method and Apparatus. (1) *Electric circuit for determining the dielectric constant.* The electric capacity was determined by the "beat method". As this method is now extensively used and is well known, its essential points alone are given in the circuit diagram of Fig. 1. In Fig. 1, I is a variable frequency oscillator circuit comprising a cell C_x to be subjected to measurement and a variable condenser of high precision C_v (capacity, 1500 $\mu\mu$F) which is arranged parallel with C_x. III is a fixed frequency (10^6C.) oscillator circuit comprising a quartz-oscillator. The beat between I and III (1000 cycles) is amplified and detected by means of II which is loosely coupled with I and III. The sound is received by a loud speaker. The whole apparatus is kept in a copper case that it may be protected from external disturbances.

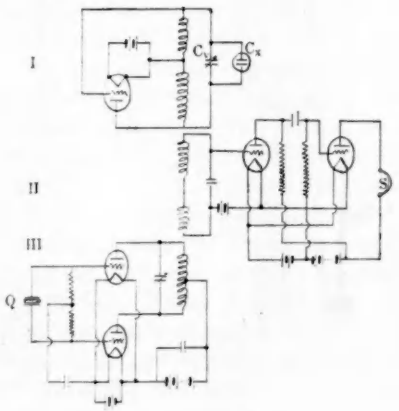


Fig. 1.

(2) *Cell.* (See Fig. 2, C) The cell consists of brass cylinders 90 mm. long and 1 mm. thick which are concentrically put one in another between the walls of a double-walled glass cylinder 39 mm. in outside diameter and 23 mm. in inside diameter. Some difficulties were encountered in working the glass so as to make it stand the low temperature. With such a device the temperature of the sample therein could be made uniform and a small amount of the sample was enough for the purpose.

Further, the cell-electrodes were gold-plated for fear of any great error being caused by a dielectric film which might have been formed on their surfaces by the action of fluorine or chlorine. Care was taken not to use them continuously for a long time. The cell had four long glass tubes for introducing lead wires and for taking in and out the sample. A quartz film pressure gauge was attached to one of the tubes. A platinum resistance thermometer R occupies the space in the centre of the cell. The capacity of the cell in the vacuous state was about 70 $\mu\mu$F.

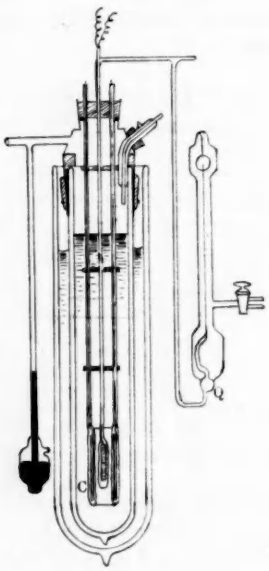


Fig. 2.

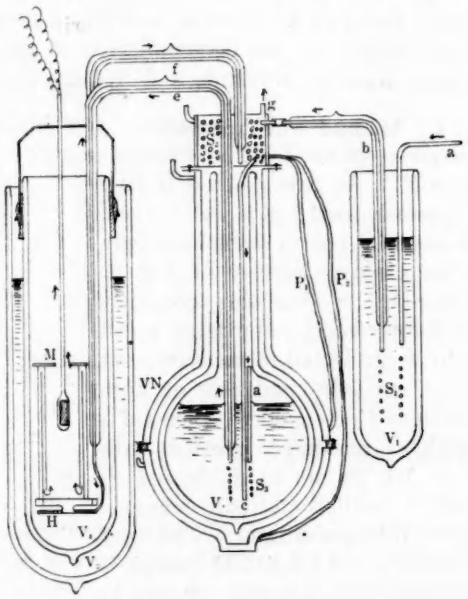


Fig. 3.

(3) *Cooling device.* Liquid nitrogen or liquid hydrogen was used for condensing the sample and for keeping the cell at a constant temperature. For keeping a constant low temperature, different devices were used according to the range of temperature of the measurement. Thus five kinds were used, which were (a) for 0° to −130°C., a device for automatically keeping a constant temperature, with pentane as the vessel liquid and indirectly cooled by liquid nitrogen, (b) for −130° to −183°C., a cryostat with vapour of liquid nitrogen as the cooling medium, (c) for −183° to −195°C., a cryostat using liquid oxygen and liquid nitrogen,

(d) for −195° to −250°C., a cryostat with vapour of liquid hydrogen as the cooling medium, (e) for −252° to −258°C., a cryostat using liquid hydrogen and solid hydrogen.

Of these, (a) and (c) have often been used in the author's experiments, and (e) is one which was used in the measurement of the specific heat of solid fluorine[1] and is outlined in Fig. 2. (b) and (d) were used for the first time.

Cryostat using hydrogen vapour. The apparatus illustrated in Fig. 3 was devised by consulting Leiden's[2]. V_1 is a Dewar vessel for liquid nitrogen, V_2 a Dewar vessel for storing and vaporizing liquid hydrogen, V_4 a cryostat containing hydrogen vapour, and V_3 a Dewar vessel containing liquid nitrogen and intended for reducing thermal conduction to V_4. Outside V_2 there is a double-walled jar V_N made of copper plate. Through the pipes P_1 and P_2 liquid nitrogen and its vapour are introduced between the walls of the jar for keeping the wall of V_2 at a low temperature. It is difficult to store liquid hydrogen for a long time on account of its very low temperature and its heat of vaporization per unit volume being very small as compared with that of liquid air (about 1/7). When V_2 was not protected by V_N, 4 litres of liquid hydrogen was vaporized in about 12 hours. When it was surrounded by V_N and kept at a low temperature with liquid nitrogen, it remained for about 18 hours.

The hydrogen gas enters at a and is cooled by the liquid nitrogen and liquid hydrogen vapour as it goes through S_1, b and S_2, and gets out in bubbles by C at the bottom of V_2. At the same time the liquid hydrogen in V_2 is vaporized. The vapour, starting from d, passes through S_3 and e and enters the spiral H near the bottom of V_4. There is a heating coil outside H, by which the temperature of the hydrogen vapour in H is adjusted. Thus the vapour goes up and down through the spacings in the triple wall of the copper cylinder over H, and finally enters the cylinder. This cylinder, intended for ensuring a uniform temperature, has a resistance thermometer. By controlling the flow of hydrogen gas and the heating of H, the temperature is adjusted. The hydrogen gas goes out by an opening in the upper part of M, and passes through the double-walled pipe f, and cooling the group of spirals S_2, gets out by g.

With this apparatus, any temperature between −195°C. and −250°C. could be kept constant with a variation of not more than 0.05°.

(4) *Determination of the density of condensed liquids.* For obtaining the molecular polarization of a liquid by measuring its dielectric con-

(1) See the eighth paper of this series.

(2) Onnes and Crommelin, *Commun. Phys. Lab. Univ. Leiden*, No. 154C (1921).

stant the density of the liquid must be determined. For this purpose an apparatus as shown in Fig. 4 was used. The whole apparatus was made of thin Pyrex glass. The volume of the capillary tube was accurately determined in advance. The test liquid was condensed in the capillary tube. The neck in the upper part of the apparatus was sealed by fusion. The temperature of the capillary tube was varied and the height of the liquid was measured by means of a comparator or cathetometer. Then the whole apparatus was brought to an ordinary temperature and the liquid was vaporized in the spherical part. Thus the weight of the sample was determined.

Table 1.

$T_{abs.}$	ρ (specific weight)	ε	P_M
87.62	1.158	1.487	3.856
78.20	1.202	1.511	3.872
68.00	1.250	1.538	3.891
59.51	1.290	1.556	3.882

Fig. 4.

II. **Results of the Measurements.** (1) *Liquid oxygen.* See Table 1. The error of the dielectric constant was in a range of ±0.1%.

The molecular polarization of oxygen could be regarded as almost independent of the temperature. Thus, m (molecular moment of liquid oxygen) = 0 could naturally be expected.

(2) *Liquid fluorine.* See Table 2. Table 2 also shows that there was no regular variation in P_M. The irregular variation was considered due to the error of measurement. Therefore the molecular moment is zero.

(3) *Liquid chlorine.* Commercial liquid chlorine, after subjected to five fractional distillations, was used (Table 3).

According to Lewis,[3] liquid chlorine also has a very small moment, which, however, could not be ascertained from the above P_M. The author

(3) Lewis, "Valence and the Structure of Atoms and Molecules"; C. Smyth, *J. Am. Chem. Soc.*, **46** (1924), 2151.

Table 2.

$T_{abs.}$	ρ	ε	P_M
57.40	1.204	1.567	5.012
60.51	1.195	1.561	5.008
64.41	1.185	1.553	4.989
68.38	1.154	1.546	5.069
73.00	1.141	1.536	5.046
75.01	1.136	1.533	5.100
79.40	1.124	1.524	5.024
83.21	1.113	1.517	5.016

Table 3.

$T_{abs.}$	ρ	ε	P_M
208.00	1.643	2.147	11.94
210.51	1.636	2.139	11.93
215.60	1.621	2.123	11.92
220.61	1.605	2.104	11.90
227.90	1.580	2.088	11.95
235.50	1.555	2.059	11.90
239.96	1.530	2.048	12.00

intends to make further determination of the dielectric constant with a dilute solution.

(4) *Hydrogen chloride.* Hydrogen chloride was prepared by dropping concentrated sulphuric acid on sodium chloride and warming of the mixture. The gas thus produced was washed with sulphuric acid. After dried with phosphorus pentoxide, the gas was liquefied and refined by repeated fractional distillation. The liquid boiled at 168°K. and freezed at 159°K.

Table 4.

$T_{abs.}$		ε	P_M
160.01	1.267	11.80	22.55
163.25	1.258	11.42	22 52
165.60	1.251	11.16	22.52
168.11	1.244	10.85	22.49
170.25	1.239	10.60	22.44
173.50	1.230	10.21	22.38
176.75	1.221	9.84	22.32
178.00	1.218	9.70	22.28
181 15	1.211	9.31	21.99
182.76	1.206	9.12	22.15

Table 5.

$T_{abs.}$	ε
101.50	11.01
106.82	11.21
112.50	11.42
121.75	11.76
130.05	12.23
136.90	12.68
140.35	13.06
149.21	13.12
153.50	13.06
9	Transition point
98.5	3.10

P_M (Table 4) clearly showed a tendency to decrease with the rise of temperature. It may be said to have a great moment. Measurements with liquid hydrogen chloride at three points between 158°K. and 165°K.

were made by Cone[4] and by Smyth,[5] but, as the ranges of temperature of their measurements were very small and the number of points of measurements also very small, no such tendency was seen in their experiments.

Measurement was also carried out with solid hydrogen chloride, Table 5. ε had at first a tendency to increase with the fall of temperature as was the case with liquid hydrogen chloride. However, this was the reverse of the tendency of normal solids. The fact shows that hydrogen chloride does not immediately form perfect crystals even when it is brought to a temperature below the freezing point, but that it ceases innermolecular rotation and makes perfect crystals only when it reaches the next transition point (99°K.).

P_M was not calculated because the density of the solid was not clear.

It will be interesting to make a study of the change in the molecular heat, especially in the electric field with reference to the result of the study on the dielectric constant, of hydrogen chloride making "Rotationsumwandlung" and of other hydrogen halides, ammonium halides, and others making similar transition.[6]

The results of measurements with O_2, F_2, Cl_2, and HCl are illustrated in Figs. 5 to 8.

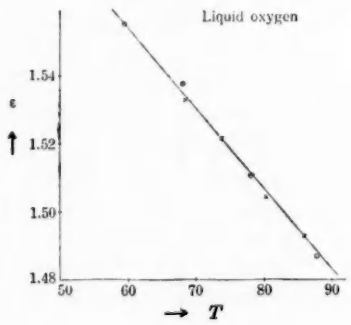


Fig. 5.

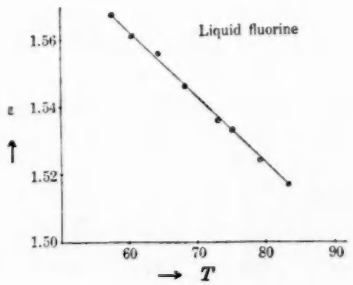


Fig. 6.

⊙ Kanda × Werner and Onnes[7]

(4) Cone, *J. Am. Chem. Soc.*, **53** (1931), 1278.

(5) Smyth, *J. Am. Chem. Soc.*, **55** (1933), 1830.

(6) Pauling, *Phys. Rev.*, **36** (1930), 480; Fowler, *Proc. Roy. Soc.* (London), A, **149** (1935), 1.

(7) Werner and Onnes, *Commun. Phys. Lab. Univ. Leiden*, No. **178C** (1926).

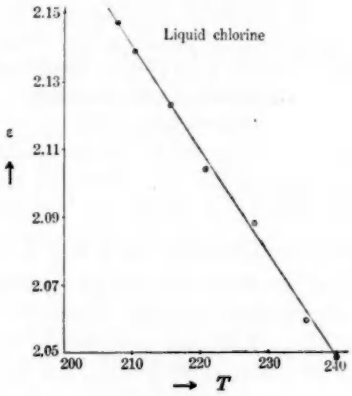


Fig. 7.

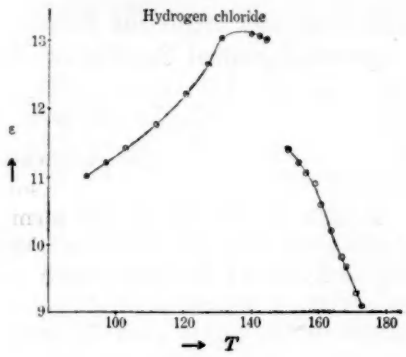


Fig. 8.

The author expresses his cordial thanks to Prof. Aoyama under whose guidance the present work was carried out and thanks are due to Prof. Mizushima of the Tokyo Imperial University, who kindly advised him through the investigation. He is also very much indebted to the Japan Society for the Promotion of Scientific Research for a grant.

Cryogenic Section,
Research Institute for Iron, Steel and Other Metals,
Tohoku Imperial University.

Studies on the Aqueous Solutions of Some Chromic Salts. I. Spectrochemical Studies of the Chloro-aquo Compounds.

By Hideo SUEDA.

(Received October 12th, 1937.)

Studies on the chromic salts were active until about 1910, but were not continued after the perfect explanation of the three isomers of chromic chloride hydrate, then discovered by A. Recoura[1] and N. Bjerrum[2], was given by Werner's co-ordination theory. For the purpose of investigating the constitution of these salts in various hydrogen ion concentrations, the author has quantitatively measured their absorption spectra in the ultra-violet region by changing the *p*H values. Such researches have not yet been systematically performed[3].

The measurements of the absorption spectra and hydrogen ion concentration are similar to those which were applied to the author's previous studies on the cobalt[4] and chromium[5] ammine-complex salts.

The absorption spectra were determined as soon as the chromic salts were dissolved, because the structural changes of these complex salts occurred after their solutions had been left standing for a long time. The thickness of the layer and the concentration of solutions were suitably chosen in the ranges of 10–50 mm. and 1/50–1/100 N (for the chromium atom), respectively. As the Lambert-Beer law holds under these conditions, $\log \varepsilon$[6] was adopted for the unit of the absorption intensity, and the details of the descriptions about the conditions of measurement were neglected. The following chromic compounds have been studied in the present work: violet chloride $[Cr(H_2O)_6]Cl_3$[7], violet sulphate $Cr_2(SO_4)_3 \cdot 17H_2O$[8], chrome alum $KCr(SO_4)_2 \cdot 12H_2O$[9], Bjerrum's salt

(1) *Compt. rend.*, **102** (1886), 548; *Ann. chim. phys.*, **10** (1887), 34.

(2) *Z. physik. Chem.*, **59** (1907), 581.

(3) A. Byk and H. Jaffe did not obtain the absorption curves, *Z. physik. Chem.*, **68** (1909), 323.

(4) This Bulletin, **10** (1935), 50, 85; **12** (1937), 71.

(5) This Bulletin, **10** (1935), 267.

(6) ε is defined from the formula: $\log I_0/I = \varepsilon cd$, where I_0 and I represent respectively the light intensity given before and after its transmission; c, concentration of solution in normal; d, layer thickness of solution in cm.

(7) N. Bjerrum, *Z. physik. Chem.*, **59** (1907), 339.

(8) R. F. Weinland and R. Krebs, *Z. anorg. allgem. Chem.*, **49** (1906), 165.

(9) Recrystallised two times below 35°C. Merck's extra pure chrome alum.

$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$[2], $[Cr(H_2O)_5Cl]SO_4$[10], green chromic chloride $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$[7]. They were prepared by referring the papers indicated in the foot notes.

I. The absorption curves and the hydrogen ion concentration of the solutions. (A) $[Cr(H_2O)_6]Cl_3$; $Cr_2(SO_4)_3 \cdot 17H_2O$; $KCr(SO_4)_2 \cdot 12H_2O$. The experiments made for the three above-mentioned salts are summarised in Table 1. Curve numbers given in the table correspond to those noted in Fig. 1.

Table 1.

	Compound	Conc.	Solvent	*p*H	Curve no.
1	$[Cr(H_2O)_6]Cl_3$	1/50 N	1/100 N HCl	1.8	I
2	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	,,	1.9	,,
3	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	1.8	,,
4	$[Cr(H_2O)_6]Cl_3$	,,	H_2O	2.7	,,
5	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	,,	2.9	,,
6	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	,,	,,
7	$[Cr(H_2O)_6]Cl_3$	,,	1/1000 N NaOH	3.1	,,
8	,,	,,	5/1000 N NaOH	3.6	II
9	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	8/1000 N NaOH	4.1	III
10	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	4.0	,,
11	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	1/100 N NaOH	4.3	,,
12	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	,,	,,
13	$[Cr(H_2O)_6]Cl_3$	1/100 N	,,	4.7	—
14	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	,,	—

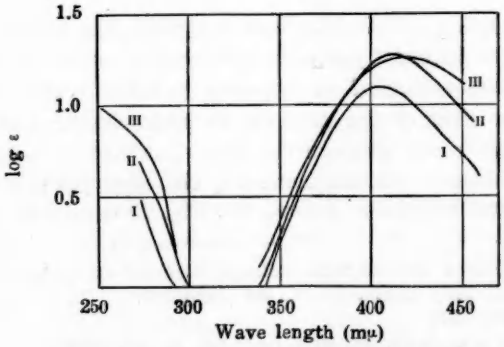


Fig. 1. The absorption spectra of $[Cr(H_2O)_6]^{+++}$

(10) R. F. Weinland and T. Schumann, *Ber.*, **40** (1907), 3091.

As the absorption spectra of the solutions 1–7 in Table 1 are almost coincident, they are shown by a curve (curve I, Fig. 1). All these solutions are bluish-violet, but they become greener with the addition of sodium hydroxide to the solution, and their absorption curves then approach curve III in Fig. 1, that is, their absorption curves shift to the longer wave length, increasing their absorption capacities.

In the solutions containing sodium hydroxide equivalent to the chromium atom (13 and 14 in Table 1), the precipitation of chromic hydroxide was recognized when ultra-violet light was projected. The precipitation began in the part where light was projected. But, it did not occur when the solution was protected from light, even under the same conditions. It can therefore be safely concluded that this reaction is accelerated by light.

As the absorption curves of these three salt solutions were almost identical[11] in the range of *p*H 1.8 and 3.1, these salts must have the same chromofore. A. Werner and A. Gubster[12] gave already formula $[Cr(H_2O)_6]Cl_3$ to the violet chromic chloride hydrate, and other researchers also confirmed their opinion[13]. This suggests that the violet chromic sulphate as well as the chrome alum should have the same complex ion with the above-mentioned violet chloride. A. Sénéchal[14] and W. R. Whitney[15] gave already formula $[Cr_2(H_2O)_{12}](SO_4)_3$ to the violet sulphate, but their confirmation for giving the formula to this salt seems to be weak. From the present results of the absorption spectra, the author wishes to give formulæ $[Cr(H_2O)_6]_2(SO_4)_3 \cdot 5H_2O$ and $K[Cr(H_2O)_6](SO_4)_2 \cdot 6H_2O$ to the violet chromic sulphate and the chrome alum respectively.

(B) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$; $[Cr(H_2O)_5Cl]SO_4$. For $[Cr(H_2O)_5Cl]Cl_2$ absorptions in three different *p*H were observed as indicated in Table 2. In this case, the absorption of the aqueous solution (curve II, Fig. 2) was not similar to that of the solution in hydrochloric acid (curve I, Fig. 2). The latter curve was, on the whole, shifted to a longer wave length than the former. On the contrary, the absorption curve of the solution with sodium hydroxide (curve III, Fig. 2) moved to the shorter

(11) The violet chloride and sulphate indicated identical curves also in the visible region, N. Bjerrum, *Z. anorg. allgem. Chem.*, **63** (1909), 140.

(12) *Ber.*, **34** (1901), 1579.

(13) P. Pascal, "Traité de Chimie Minérale," Vol. X, 1021 (1933).

(14) *Compt. rend.*, **156** (1913), 552.

(15) *Z. physik. Chem.*, **20** (1896), 40.

Table 2.

Compound	Conc.	Solvent	*p*H	Curve no.
$[Cr(H_2O)_5Cl]Cl_2$	1/70 N	1/100 N HCl	1.9	I
,,	1/58 N	H_2O	3.2	II
,,	1/72 N	1/100 N NaOH	4.3	III
,,	1/110 N	9/1000 N NaOH	4.7	—
$[Cr(H_2O)_5Cl]SO_4$	1/50 N	1/100 N HCl	2.0	IV
,,	,,	H_2O	2.9	,,
,,	,,	8/1000 N NaOH	4.1	V
,,	,,	1/100 N NaOH	4.2	,,

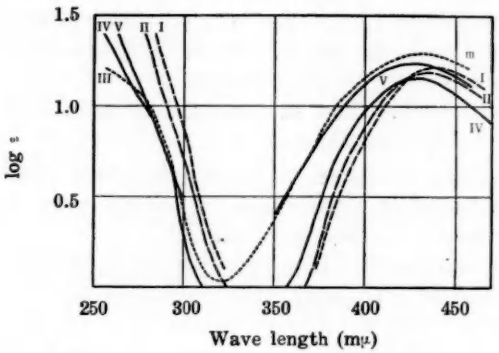


Fig. 2. The absorption spectra of $[Cr(H_2O)_5Cl]^{++}$

wave length[16]. A precipitate of chromic hydroxide was observed in the solution of *p*H 4.7, when it was exposed to light.

As $[Cr(H_2O)_5Cl]Cl_2$ is very hygroscopic and unstable, the complex ion $[Cr(H_2O)_5Cl]^{++}$ cannot be easily studied by its absorption spectra. Similar experiments were therefore repeated with the sulphate which is more stable than the chloride. The absorption curve given by the aqueous solution of the sulphate (curve IV, Fig. 2) was identical with that observed with the solution in hydrochloric acid. The solution of this salt with sodium hydroxide showed similar absorption curves (curve V, Fig. 2) when *p*H was 4.1 and 4.2.

(16) Except hydroxo-compounds, among the salts already studied by the author, this salt is the only one that shows different absorption spectra in neutral and in acidic solutions.

The wave length representing the absorption band of curve V, Fig. 2 almost coincides with curve IV, and the intensity observed in the former curve is a little stronger than that shown by the latter. But, the absorptions in the range of shorter wave length (near 300 mμ) were observed to be quite similar in these two curves. A few minutes after the end of the measurement, a precipitation of chromic hydroxide occurred in the solution of *p*H 4.2.

From the fact that the chloride and the sulphate show different absorptions in spite of the same complex ion, it can be safely assumed that either of these two salts is impure. As the chloride is unstable in solution as well as in the solid state, it can be naturally supposed to be impure. If the impurity is based on $[Cr(H_2O)_4Cl_2]Cl$ which is prepared by the transformation of $[Cr(H_2O)_5Cl]Cl_2$, the anormality in the absorption can be easily explained by assuming that the transformation of Bjerrum's salt into the green chloride is more rapid in hydrochloric acid than in the neutral aqueous solution.

(C) $[Cr(H_2O)_4Cl_2]Cl$. The results obtained with this compound are summarised in Table 3 and Fig. 3.

When the *p*H-value increased in the solution, the absorption was generally shifted to the shorter wave length, accompanying the increase of the absorption capacity in the absorption band.

As seen in (A), (B) and (C), the absorption curves shown by solutions of higher *p*H-values are similar with one another.

Table 3.

Conc.	Solvent	*p*H	Curve no.
1/50 N	1/100 N HCl	1.9	I
,,	H_2O	3.3	I
1/100 N	8/1000 N NaOH	4.3	II
,,	1/100 N NaOH	4.6	III

Table 4.

Compound	$\lambda_{max.}$ (mμ)	lo
$[Cr(H_2O)_6]^{+++}$	405	1.10
$[Cr(H_2O)_5Cl]^{++}$	430	1.15
$[Cr(H_2O)_4Cl_2]^{+}$	443	1.24

Table 5.

The Absorption of $[Cr(H_2O)_4Cl_2]Cl$.

λ (mμ)	ε	
	(obs.)	(calc.)
400	6.8	6.3
410	10.0	11.1
420	13.2	15.9
430	15.8	19.2
440	17.4	20.1
450	16.6	17.9
460	15.1	15.3

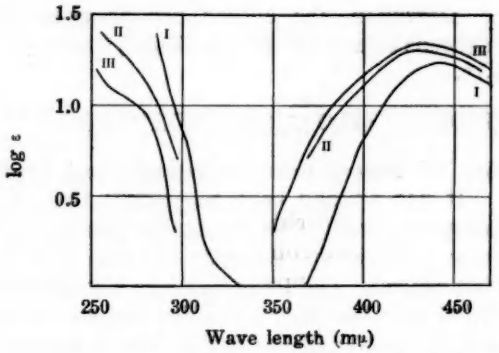


Fig. 3. The absorption spectra of $[Cr(H_2O)_4Cl_2]Cl$

II. Action of alkali on the aqueous solutions of aquo-chloro chromic salts. By the thorough investigations of the aqueous solution of violet chloride, N. Bjerrum[7] confirmed the existence of the following equilibrium, and the equilibrium constant has been already determined by many authors[17]:

$$[Cr(H_2O)_6]^{+++} \rightleftarrows [Cr(H_2O)_5OH]^{++} + H^+.$$

When sodium hydroxide is added to the aqueous solution of this salt, $[Cr(H_2O)_5OH]^{++}$ must be formed, and it is quite natural that the absorption given by its solution of high *p*H is more similar with that given by $[Cr(H_2O)_5OH]^{++}$.

As to the aqueous solution of $[Cr(H_2O)_4Cl_2]Cl$, the following hydrolysis was suggested by A. B. Lamb[18], who already measured its equilibrium constant[19].

$$[Cr(H_2O)_4Cl_2]^+ + 2H_2O \rightleftarrows [Cr(H_2O)_5OH]^{++} + H^+ + 2Cl^-.$$

For the aqueous solution of $[Cr(H_2O)_5Cl]^{++}$, the hydrolysis has not yet been reported. As the absorption given by a solution of higher *p*H-value of this salt becomes almost the same as that represented by the solutions of $[Cr(H_2O)_6]^{+++}$ and $[Cr(H_2O)_4Cl_2]^+$ with sodium hydroxide, the addition of alkali to the solution of $[Cr(H_2O)_5Cl]^{++}$ tends to form

(17) N. Bjerrum, *Z. physik. Chem.*, **59** (1907), 339; A. B. Lamb and G. R. Fonda, *J. Am. Chem. Soc.*, **43** (1921), 1154; H. G. Denham, *J. Chem. Soc.*, **93** (1908), 53; J. N. Brönsted and K. Volgvartz, *Z. physik. Chem.*, **134** (1928), 97.

(18) *J. Am. Chem Soc.*, **28** (1906), 1710.

(19) A. B. Lamb and G. R. Fonda, *J. Am. Chem. Soc.*, **43** (1921), 1154.

$[Cr(H_2O)_5OH]^{++}$. Hereupon, the author has assumed the following equilibrium in the aqueous solution of $[Cr(H_2O)_5Cl]^{++}$ like $[Cr(H_2O)_6]^{+++}$ and $[Cr(H_2O)_4Cl_2]^{+}$.

$$[Cr(H_2O)_5Cl]^{++} + H_2O \rightleftarrows [Cr(H_2O)_5OH]^{++} + HCl.$$

III. Absorption of aquo-chloro compounds and configuration of $[Cr(H_2O)_4Cl_2]Cl$. It has already been reported[5] that the absorption curve near 250 $m\mu$, given by the chloro-ammine chromic complex salts, is regularly shifted to a longer wave length, as often as a chlorine atom enters into a complex radical. The same fact was also observed with this chloro-aquo salt, that is, the wave lengths, where $[Cr(H_2O)_6]^{+++}$, $[Cr(H_2O)_5Cl]^{++}$, and $[Cr(H_2O)_4Cl_2]^{+}$absorbed the light by the intensity of $\log\varepsilon = 0.5$, were 273 $m\mu$, 296 $m\mu$, and 307 $m\mu$.

The wave lengths and extinction coefficients of the maximum absorptions of these three salts have a certain relation with the number of chlorine atoms in a complex radical, and as indicated in Table 4, they are shifted in a definite direction in proportion to the number of chlorine atoms.

From the point of view of Werner's co-ordination theory, there should be two isomers of $[Cr(H_2O)_4Cl_2]Cl$, i.e. cis and trans. But, it has not yet been determined whether the ordinary salt has cis- or trans-configuration. Applying to this salt the hypothesis[20], which the present author already proposed, and assuming this salt to have cis-form, he has calculated the absorption of $[Cr(H_2O)_4Cl_2]^{+}$ from absorption curves given by $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]SO_4$. The calculated values show a coincidence with the observed values to the extent indicated in Table 5. But, from this comparison of values only, the author cannot give a cis-configuration to this salt, because when this salt is assumed to be trans, a better coincidence might be obtained by calculation, which, however, has as yet been impossible.

Summary.

(1) The absorption spectra of six solutions of chromic chloride and sulphate hydrates were quantitatively measured in the ultra-violet region.

(2) Violet chromic sulphate and chrome alum should respectively have the formula $[Cr(H_2O)_6]_2(SO_4)_3$ and $K[Cr(H_2O)_6](SO_4)_2$.

(20) The hypothesis is related to the configuration of complex salts and their absorption spectra; this Bulletin, **12** (1937), 188.

(3) Chloro-aquo chromic salts were transformed into the hydroxo-pentaquo chromic salts in the solutions where the *p*H-values were higher than 4.0.

(4) The substitution of a chlorine atom for a molecule of water in these salts caused the absorption band to shift in the direction of the increasing wave length and absorption capacity.

(5) Following his method, the author has made a comparison of calculated and observed values of the absorption of green chromic chloride.

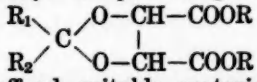
In conclusion, the author wishes to express his sincere thanks to Assist. Prof. T. Uemura of the Tokyo University of Engineering for his kind encouragement.

Laboratory of Inorganic Chemistry,
Tokyo University of Engineering (Tokyo Kōgyō-Daigaku).

Condensation of Diethyl Tartrate with Cyclic Ketones and the Molecular Rotation of the Resulting Compounds.*

By Yojiro TSUZUKI.

(Received October 23rd, 1937.)

It was reported in the previous papers[1] that alkyl tartrates can be condensed with some simple carbonyl compounds giving bridged derivatives of tartaric acid of the type  , and was shown that these compounds would afford suitable materials for the study of the optical activity of tartaric acid. Thus it was pointed out that the molecular rotation of these compounds shows a certain regularity, i.e. the power of the strong lævo-rotation of these compounds falls off as the bulk of the radicals R_1 and R_2 increases, and on the other hand it increases with the increasing bulk of the radical R. And further the rotatory dispersion of these bridged derivatives of tartaric acid was in-

* Synthesis of bridged derivatives of tartaric acid and their optical activity. IV.

(1) Y. Tsuzuki, this Bulletin, **10** (1935), 255; **11** (1936), 362.

vestigated, with a view to interpret the complex nature of the optical activity of tartaric acid and of its derivatives, the results of which brought out a suggesting relation between the radicals R_1 and R_2 and the optically active absorption bands of the compounds.[2] The number of these compounds are, however, very small, so that materials must be substantiated, in order to consolidate the above statement. The present paper aimes to supply some materials for this purpose and to give some simple suggestion of the tendency of the molecular rotation of the newly synthesized bridged compounds. The author has, in the first place, prepared condensation products with one cyclic radical instead of the separate two radicals R_1 and R_2 which were contained in the already synthesized compounds.

Condensation. Diethyl tartrate has been condensed with the following cyclic ketones: cyclopentanone, cyclohexanone, *o*-methylcyclohexanone, *m*-methylcyclohexanone, and *p*-methylcyclohexanone. Cyclopentanone was prepared by distilling adipic acid with barium hydroxide at 315–320°. The three methylcyclohexanones were prepared by oxidising the corresponding alcohols with Beckmann's mixture. *o*-Methyl- and *m*-methylcyclohexanols were Takeda samples and *p*-compound[3] was prepared from *p*-cresol by catalytic hydrogenation. Cyclopentanone, b.p. 128.5–129.5° (760 mm.), $n_D^{20} = 1.4358$. Cyclohexanone, b.p. 153–154° (760 mm.), $n_D^{20} = 1.4506$. *o*-Methylcyclohexanone, b.p. 164° (760 mm.), $n_D^{20} = 1.4482$. *m*-Methylcyclohexanone, b.p. 165° (755 mm.), $n_D^{20} = 1.4482$. *p*-Methylcyclohexanone, b.p. 163–164° (751 mm.), $n_D^{20} = 1.4448$.

The condensation reaction proceeds very smoothly in every case. The yield is fairly good, from 50 to 70% of the theoretical amount. The purification of the condensation product is easy. As the condensation reagent phosphorus pentoxide was employed exclusively, which proved to be very useful, but in the reactions[1] previously performed, various condensation reagents had to be applied according to the nature of the carbonyl compound.[2]

The condensation and the purification of the product has been carried out in the following way: to the mixture of diethyl tartrate (1/20 mol) and cyclic ketone (1/20 mol) is added in portions 10 g. phosphorus pentoxide at 80–90°, in the course of 30–60 minutes. The solid phase of the phosphorus pentoxide is coloured quite strongly, but the liquid mixture remains almost colourless, only in some cases faintly yellowish coloured. In the case of higher members of the ketone homologue the

(2) Y. Tsuzuki, this Bulletin, **11** (1936), 586.

(3) The author is grateful to Dr. K. Ishimura who kindly afforded this material.

temperature must be raised comparatively higher and the duration of reaction must be prolonged. After the whole of phosphorus pentoxide has been added, the heating of the reaction mixture is further continued at that temperature for 30–60 minutes, with occasional stirring. Then the liquid mixture is decanted from the phosphorus pentoxide portion and evaporated at 130° under the pressure 20–30 mm., by which process the unchanged ketone distils over. The product is dissolved in 70 c.c. ether. The ethereal solution is shaken 4 times with each 30 c.c. saturated aqueous solution of borax, whereby the unchanged ethyl tartrate can be almost completely removed into the borax layer, and further shaken with water and dried with anhydrous sodium sulphate. After the ether was evaporated off, the remaining liquid is distilled under reduced pressure.

Reaction products. The condensation products thus obtained and purified are all transparent colourless liquid, but they show some pale yellowish colouration when freshly distilled, which fades away on standing for a few days. This is probably due to some similar cause of the phenomenon, which was observed by Patterson long ago in the case of diethyl tartrate—green colouration produced by its vacuum distillation and disappearance of the colour on its standing—and quite recently given a plausible explanation by the same author.[4]

The physical constants of the new condensation products thus obtained will not be individually described, but are put into Table 1, together with the analytical data.

Molecular rotation. As seen in Table 2 the molecular rotation of the condensation product decreases in magnitude with the increasing bulk of the ketone-residue in the compound, thus the molecular rotation of diethyl cyclopentylidene-tartrate is smaller than that of diethyl isopropylidene-tartrate, but larger than that of diethyl cyclohexylidene-tartrate.

These facts will be understood by the molecular theory of de Malleman[5] as well as of Boys[6], who regards the volumes of the radicals as a dominating factor of the optical activity. In fact the molecular rotation goes almost inversely proportional with the parachor, a quantity equivalent to the molecular volume of the radical.

(4) T. S. Patterson, *J. Chem. Soc.*, **121** (1922), 1042; T. S. Patterson and A. H. Lamberton, *J. Chem. Soc.*, **1937**, 963.

(5) *Trans. Faraday Soc.*, **26** (1930), 281.

(6) *Proc. Roy. Soc.* (London), A, **144** (1934), 655.

Table 1. The Physical Constants and the Analytical Data of the Bridged Derivatives of Tartaric Acid Obtained by Condensing Diethyl Tartrate with Cyclic Ketones.

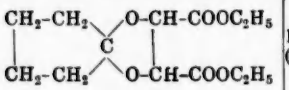
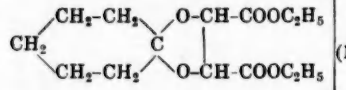
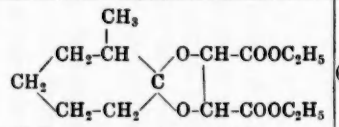
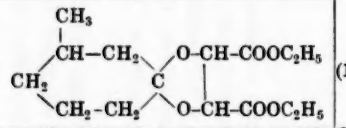
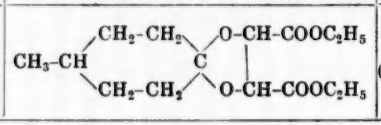
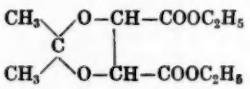
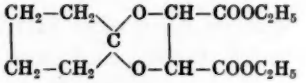
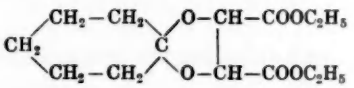
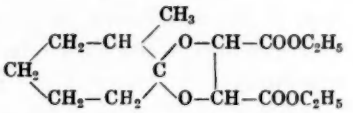
Substance	Structural Formula	Boiling Point (corr.)	d_4^{20}	n_D^{20}	Molecular Refraction	$[\alpha]_D^{20}$	$[M]_D^{20}$	Elementary Analysis		Yield (%)
								Found	Calc.	
Diethyl cyclopentylidene-tartrate		170–171° (12 mm.)	1.1468	1.4560	obs. 64.50 calc. 64.44	−40.55°	−110.4°	C 57.07 H 7.35	C 57.31 H 7.41	49
Diethyl cyclohexylidene-tartrate		178° (12 mm.)	1.1329	1.4605	obs. 69.25 calc. 69.05	−35.57°	−101.8°	C 58.63 H 7.77	C 58.70 H 7.75	51
Diethyl *o*-methylcyclohexylidene-tartrate		184° (14 mm.)	1.1140	1.4590	obs. 73.66 calc. 73.66	−21.81°	−65.48°	C 59.63 H 8.11	C 59.96 H 8.06	52
Diethyl *m*-methylcyclohexylidene-tartrate		186° (14 mm.)	1.1085	1.4572	obs. 73.78 calc. 73.66	−35.42°	−106.3°	C 59.73 H 7.96	C 59.96 H 8.06	61
Diethyl *p*-methylcyclohexylidene-tartrate		188° (14 mm.)	1.1109	1.4580	obs. 73.73 calc. 73.66	−30.49°	−91.53°	C 59.66 H 8.06	C 59.96 H 8.06	69

Table 2. Molecular Rotation and Parachor of the Condensation Products.

	Molecular Rotation at 20°	Parachor of Ketone-residue
	−120.9°	117.0
	−110.4°	160.8
	−101.8°	199.8
	−65.48°	238.8

The introduction of one methyl group in the cyclohexylidene residue tends to decrease the molecular rotation of the resulting compound. But it is seen that the position of a substituent exerts a great influence on the molecular rotation. The ortho-position has the most diminishing effect, while the meta-position has the least effect, rather an increasing effect. Although these methylcyclohexylidene residues may have the same magnitude of parachor, but their volumes effective to the asymmetric carbon atoms of the compounds must be different. The nearest ortho-position exerts a most intense influence and the meta-position at the least. In the flexible cyclohexane-ring structure of Sachse and Mohr the group attached to the meta-position is situated a little farther than that of the para-position. The differences of these influences by position are, however, quite remarkable, so that the electronic effect due to the position of a group must also be considered in these cases, in order to comprehend more satisfactorily the molecular rotation. Similar phenomena of the effects of position have been already known in the absorption of light in

aromatic compounds, where the ortho effect is largest and the meta effect is least or none.[7] These facts would be understood by the electronic theory of aromatic substitution.

Summary.

(1) It has been shown that the condensation of diethyl tartrate with cyclic ketones can be effected with great ease by the use of phosphorus pentoxide as condensation reagent.

(2) New products obtained by condensing diethyl tartrate with cyclic ketones, namely cyclopentanone, cyclohexanone, and three isomeric methylcyclohexanones, have been described, and their physical constants have been compared in a table.

(3) The molecular rotation of these homologous compounds decreases as the parachor of the ketone-residue in the condensation product increases, but the influence by the position of the substituent is noticed: the substitution of a methyl group at ortho-position is the most effective, and that of meta-position is nearly ineffective.

Musashi Higher School,
Naka-arai, Tokyo.

(7) Y. Shibata, *Acta Phytochim.* (Japan), **1** (1923), 91; S. Hattori, *ibid.*, **6** (1932), 131.

An Isomer of Cymene from Camphor.

By Irwin A. PEARL and William M. DEHN.

(Received October 26th, 1937.)

Cymene in 50–60% yields has been obtained from camphor by treatment with phosphorus pentoxide.[1] We have found that prolonged heating with 85% phosphoric acid,[2] gives as the large fraction, an isomer of cymene, but little or no cymene.

The theoretical isomers of cymene are and those with double bonds indicated by the following numbers:

I. 1, 3, 8(9)	V. 2, 5, 1(7)	IX. 3, 5, 1(7)
II. 1, 4, 8(9)	VI. 2, 5, 4(8)	X. 3, 5, 8(9)
III. 1, 5, 8(9)	VII. 2, 5, 8(9)	XI. 5, 1(7), 4(8)
IV. 1, 5, 4(8)	VIII. 3, 1(7), 8(9)	XII. 5, 1(7), 8(9)

and of these only III, X, and XII contain asymmetrical carbon atoms. Since our large fraction boiled at 180–182°, possessed the formula $C_{10}H_{14}$ and a specific rotation of 6.82°, it must be one of these three:

III. X. XII.

Since it agrees more closely in boiling point with *p*-menthadiene (b.p. 184°) than with limonene (b.p. 176.5°), formula X or 1-methyl-4-isopropenyl-cyclohexadiene-(2,4) is indicated.

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(1) Fittica, *Ann.*, **172** (1874), 307.

(2) Dehn and Jackson, *J. Am. Chem. Soc.*, **55** (1933), 4284. These authors showed that phosphoric acid (85%) yields hydrocarbons from certain oxygenated terpenes etc.

p-Menthadiene.

Limonene.

Formula XII is surely excluded for the reason that methylene groups attached directly to the ring are unstable in the presence of acids. Formula III is probably excluded on the basis of Horiuchi's[3] isomer (b.p. 183–186°) formed by the dehydration of citral. Though he reports no optical activity, he assigns to his isomer formula II or III. Wallach[4] also reports an isomer of cymene (b.p. 183°) derived from limonene tribromide, but assigns to it no structural formula.

Experimental.

A mixture of 340 g. of camphor and 290 g. of 85% phosphoric acid in a flask was heated under a reflux air condenser in an oil bath heated at 200° for about 7 hours after all the camphor had liquefied. The mixture was then distilled with steam. The distillate was extracted with ether and the ether was evaporated. Some of the unchanged camphor that came over with the steam was separated from the oil by freezing out in a salt-ice mixture and filtering. A trace of camphor that remained was transformed into cymene by repeated distilling over phosphorus pentoxide. The yield of oil was 75 g. or about 25% of the theoretical. The oil was then fractionated eleven times giving the following fractions: below 176°, 3 c.c.; 176–178°, 2; 178–180°, 13; 180–182°, 20; 182–184°, 2; 184–186°, 6; 186–188°, 2; 188–190°, 3; 190–192°, 8; 192–194°, 2; 194–196°, 2; 196–198°, 2; 198–200°, 3; above 200°, 10.

Evidently longer refluxing would have yielded more oil because both camphor and phosphoric acid were contained in the mixture.

Fraction boiling at 180–182° was analysed (Found: C, 89.27; H, 10.77. Calc. for $C_{10}H_{14}$: C, 89.48; H, 10.52%). Its odour was different from that of cymene. At 22° its refractive index was $n_a = 1.4874$; its specific rotation was $[\alpha]_D = 6.94°$; its specific gravity was 0.875.

That cymene was not first formed by the dehydration of camphor was proved by an experiment in which cymene itself was refluxed for 5 hours with 85% phosphoric acid; it was recovered unchanged at its lower boiling point.

Department of Chemistry and Chemical Engineering,
University of Washington,
Seattle, Washington.

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(3) Horiuchi, *Mem. Coll. Sci., Kyoto Imp. Univ.*, A, **11** (1928), 171.
(4) Wallach, *Ann.*, **264** (1891), 27. This isomer at 20° has a refractive index of $n_D = 1.49693$ and a specific gravity of 0.863. No optical activity was reported.

The Photochemical Dehydrogenation of 7-Dehydrocholesterol and the Pyrolysis of the Product.

By Yoshiyuki URUSHIBARA and Toshio ANDO.

(Received October 29th, 1937.)

In a preliminary note[1] the authors reported that the photochemical dehydrogenation of 7-dehydrocholesterol (I) yielded a dimolecular derivative ("pinacone") analogous to ergopinacone from ergosterol. Nearly at the same time F. Schenck, K. Buchholz, and O. Wiese[2] published a paper on the studies of 7-dehydrocholesterol, in which they described "7-dehydrocholesterol-pinacone" obtained from 7-dehydrocholesterol by a method similar to, but not identical with, that by which the present authors dehydrogenated 7-dehydrocholesterol (see the experimental part). However, the "pinacone" of the German investigators melted at 196–197°, higher by about 10° than the present authors' "pinacone". The German investigators gave to their "pinacone" a formula with one and a half molecules of water: $C_{54}H_{86}O_2 + 1\frac{1}{2}H_2O$.

The present authors repeated the dehydrogenation of 7-dehydrocholesterol by the same method as before and obtained the same results. The "pinacone", recrystallized from benzene-alcohol, had formula $C_{54}H_{86}O_2 + H_2O$ and melted at 184–185° (corr.) with decomposition. The substance dried in vacuum at 110° had formula $C_{54}H_{86}O_2$ and melted at 185.5–186° (corr.) with decomposition.

The "pinacone" was subjected to pyrolytic decomposition followed by distillation in high vacuum. The distillate obtained in a yield of 70–78% was a viscous greenish yellow oil which crystallized with difficulty. Recrystallized from methanol, the substance formed small long plates melting at 110–111° (corr.). Its 3,5-dinitrobenzoate formed light-yellow small plates melting at 210.5–211° (corr.). Analyses showed the substance was 10-desmethyl-cholestatrienol-(3) (II), analogous to neoergosterol from ergopinacone.

Schenck and co-workers, by boiling their "pinacone" with acetic anhydride and saponifying the uncrystallizable product with potash in

(1) Y. Urushibara and T. Ando, this Bulletin, **11** (1936), 802.
(2) *Ber.*, **69** (1936), 2696.

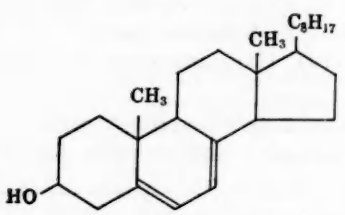
methanol, obtained "norsterol" melting at 111°. Its 3,5-dinitrobenzoate melted at 207° with decomposition.

As indicated in the accompanying table, the substances obtained by the present authors and the corresponding substances described by the German investigators show similar properties except the melting points of the "pinacone". However, it cannot be decided whether or not they are identical each with each.

Schenck, Buchholz, and Wiese			Urushibara and Ando		
Substance	Melting point	$[\alpha]_D$	Substance	Melting point	$[\alpha]_D$
"Pinacone" $C_{54}H_{86}O_2+1\frac{1}{2}H_2O$	196–197°	−181.6°(22°) in C_5H_5N	"Pinacone" $C_{54}H_{86}O_2+H_2O$ $C_{54}H_{86}O_2$	184–185° (corr.) 185.5–186° (corr.)	−171°(18°) in C_5H_5N
Norsterol	111°	+1.6°(22°) in $CHCl_3$	10-Desmethyl-cholesta-trienol-(3)	110–111° (corr.)	Nearly null in $CHCl_3$
3,5-Dinitro-benzoate of the above	207°	−2.5°(22°) in $CHCl_3$	3,5-Dinitro-benzoate of the above	210.5–211° (corr.)	−3.8°(17°) in $CHCl_3$

Dehydrogenation of 7-dehydrocholesteryl benzoate by the same method yielded the dibenzoate of the "pinacone", $C_{68}H_{94}O_4$, which, recrystallized from benzene-alcohol, formed colourless needles melting at 183–183.5° (corr.) with gas evolution. On mixing it with the free "pinacone" a depression of the melting point was observed.

While the free "pinacone" does not keep long, its dibenzoate is so stable that no change was observed in six months.



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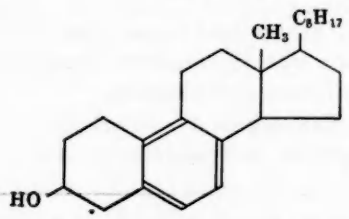

II

Experimental.

7-Dehydrocholesterol. Prepared according to the directions of A. Windaus, H. Lettré and F. Schenck.[3] Recrystallized from ether-methanol, colourless needles, m.p. 143–146.5° (corr.). The 3,5-dinitrobenzoate, recrystallized from chloroform-acetone, formed yellow needles, m.p. 212–212.5° (corr.) with decomposition[4] (Found for the dinitrobenzoate dried over phosphorus pentoxide in vacuum at 110°: C, 70.68; H, 8.28; N, 4.76. Calculated for $C_{34}H_{46}O_6N_2$: C, 70.55; H, 8.02; N, 4.84%).

"Pinacone" from 7-dehydrocholesterol. 7-Dehydrocholesterol was dehydrogenated according to the directions of H. H. Inhoffen[5] for the preparation of ergopinacone from ergosterol: 7-Dehydrocholesterol and an equal amount of eosin (Eosin, spiritlöslich, Dr. G. Grübler and Co., Leipzig) were dissolved in a mixture of 95% alcohol and a small amount of benzene. The solution was boiled thoroughly to remove air,[6] and exposed to the sun for two weeks in exclusion of air. The crystalline precipitate was collected, boiled with alcohol, and recrystallized from benzene-alcohol. Colourless thin needles, m.p. 180.5–181.5° (uncorr.) or 184–185° (corr.) with decomposition (Found: C, 82.19; H, 11.04. Calculated for $C_{54}H_{86}O_2 + H_2O$: C, 82.58; H, 11.31%). On being dried over phosphorus pentoxide in vacuum at 110°, the substance gave up the combined water (Found: H_2O, 2.06. Calculated for $C_{54}H_{86}O_2 + H_2O$: H_2O, 2.29%). The dried substance melted at 185.5–186° (corr.) with decomposition (Found: C, 84.37; H, 11.29. Calculated for $C_{54}H_{86}O_2$: C, 84.53; H, 11.31%). $[\alpha]_D^{18°} = -171°$ (9.2 mg. of the dried substance in 1 c.c. pyridine solution, $l = 1$ dm., $\alpha_D^{18°} = -1.57°$).

The "pinacone" was decomposed by keeping.

10-Desmethyl-cholestatrienol-(3) and its 3,5-dinitrobenzoate. The "pinacone" was heated at 175° under the pressure of 0.28 mm. for 15 minutes, and immediately distilled at 210–250° under 0.004–0.0015 mm. The distillate (yield 70%), forming a viscous greenish yellow oil, was heated for 30 minutes with 3,5-dinitrobenzoyl chloride and pyridine. The crystals separating out on adding water to the reaction mixture were washed with dilute acetic acid and with water, boiled with dilute acetone, and recrystallized repeatedly from benzene-methanol. Glittering light-yellow small plates, m.p. 206.5–207° (uncorr.) or 210.5–211° (corr.) (Found: C, 70.66; H, 7.42; N, 4.94. Calculated for $C_{35}H_{42}O_6N_2$: C, 70.44; H, 7.53; N, 4.98%). $[\alpha]_D^{17°} = -3.8°$ (13.3 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{17°} = -0.05°$).

In another experiment of pyrolysis, the "pinacone" was heated at 185°, 0.25 mm., for 20 minutes, and distilled at 210–260°, 0.0035–0.0008 mm., in the course of 10

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(3) *Ann.*, **520** (1935), 98.

(4) Windaus and co-workers give m.p. 207°.

(5) *Ann.*, **497** (1932), 130.

(6) Schenck and co-workers removed air from the alcoholic solution (with no benzene) of 7-dehydrocholesterol and eosin by passing carbon dioxide.

minutes. The distillate (78%) forming a viscous light greenish yellow oil solidified to an opaque yellowish mass. It was collected with ether, the ether was evaporated, and the residue was brought to crystallization by rubbing with methanol. The substance was recrystallized repeatedly from methanol. Colourless glittering small long plates, m.p. 109–110° (uncorr.) or 110–111° (corr.). $[\alpha]_D^{15°}$ = nearly null (6.7 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{15°} = \pm 0.01°$). For analysis the substance was dried over phosphorus pentoxide in vacuum at 76° (Found: C, 84.60; H, 10.86. Calculated for $C_{29}H_{40}O$: C, 84.72; H, 10.95%).

The 3,5-dinitrobenzoate prepared from the purified 10-desmethyl compound was identical with the above specimen obtained from the crude oily distillate.

The dibenzoate of the "pinacone" from 7-dehydrocholesteryl benzoate. 7-Dehydrocholesteryl benzoate (m.p. 141–142.5°, clear at 187°, corr.) was dehydrogenated in the same manner as described above. The product depositing in needles was collected, boiled with alcohol, and recrystallized from benzene-alcohol. Colourless needles, m.p. 183–183.5° (corr.) with gas evolution (Found: C, 84.03; H, 10.01. Calculated for $C_{68}H_{94}O_4$: C, 83.70; H, 9.72%). $[\alpha]_D^{17°} = -114°$ (11.9 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{17°} = -1.36°$). In admixture with the free "pinacone" the dibenzoate showed a depression of the melting point. The substance is stable in air, no change being observed in six months.

The authors express their hearty thanks to Mr. Yasohachi Yamaguchi for his generous support of this work.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

The Effects of Oxygen and Peroxides on the Rate of Addition of Bromine to Cinnamic Acid in Carbon Tetrachloride.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received October 30th, 1937.)

I. The Effect of Oxygen. In the previous paper on the same subject[1] the authors showed the relation between the extent of addition of bromine to cinnamic acid in carbon tetrachloride and the amount of oxygen present. The extent of addition in vacuum, however, was rather too small (about 60%) in view of the observation of W. H. Bauer and F. Daniels[2] that the addition was so rapid in absence of oxygen that the rate of reaction could not be measured conveniently. Then it was suspected that dissolved oxygen might not have been removed completely by the process of evacuation under cooling in liquid air. Hence, experiments were repeated by a procedure which differed from the previous method only in that a part of the solvent was evaporated in vacuum in order to remove dissolved oxygen.

Materials used in the experiments were prepared by treating commercial products as follows: Cinnamic acid was recrystallized from alcohol, melting point 133°. Bromine was refluxed with the addition of potassium bromide, distilled, shaken with concentrated sulphuric acid, and redistilled. Carbon tetrachloride was refluxed with an alkaline aqueous solution of potassium permanganate for two days, washed with water, dried over calcium chloride, distilled, and redistilled with the addition of phosphorus pentoxide on the day of use. Oxygen from the bomb was dried with calcium chloride and then with phosphorus pentoxide.

The experimental procedure was as follows: One millimol (0.1481 g.) of cinnamic acid was taken in a reaction tube of Pyrex glass with a capacity of 140 c.c., and dissolved in 40 c.c. of carbon tetrachloride. A sealed small glass bulb containing a slight excess of bromine was slipped into the tube. The tube was evacuated by a vacuum-pump at room temperature until 10 c.c. of carbon tetrachloride distilled over, 30 c.c. being left in the tube, then cooled in liquid air, evacuation being continued, and sealed off with or without admission of oxygen. The contents were melted and mixed well by shaking. The bromine bulb was broken usually

(1) This Bulletin, **12** (1937), 356.
(2) *J. Am. Chem. Soc.*, **56** (1934), 2014.

on freezing the contents of the reaction tube in liquid air, otherwise on shaking. The tube was placed in the dark at room temperature for 22 hours. An excess of aqueous potassium iodide was added to the reaction mixture, and the liberated iodine was titrated with N/10 sodium thiosulphate. The extent of addition in percentage to the cinnamic acid used was determined from the amount of bromine consumed. When the extent of addition was greater than 60%, the crystals of cinnamic acid dibromide (melting point 198°, corr.) appeared in the reaction mixture.

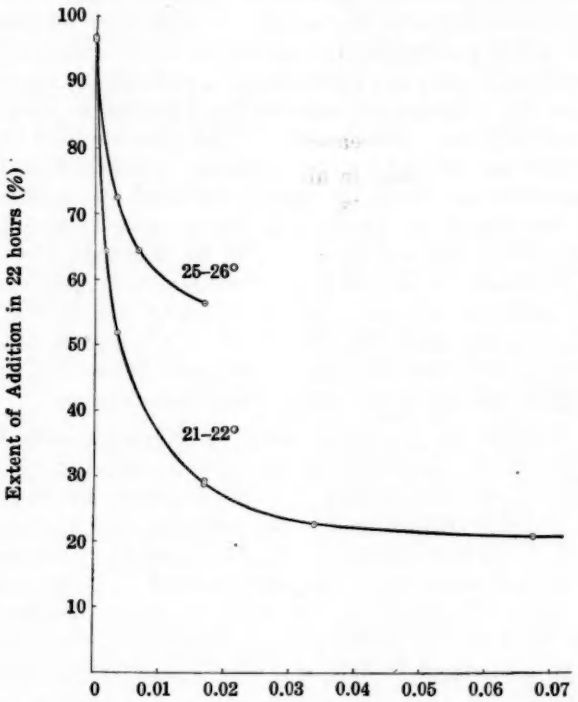
The temperatures recorded in all the tables given below are those at the beginning of the experiments. Additions of the same groups were carried out simultaneously, and thus under the same conditions. Only the experiments that belong to the same groups are strictly comparable.

Table 1.

Group of exp.	No. of exp.	Temp. (°C.)	Bromine (g.)	Amount of oxygen		Extent of addition (%)
				Admitted (c.c., n.p.t.)	Dissolved in CCl_4 solution (millimol)	
I	1	26	0.1820	0	0	96.9
	2	26	0.1798	1.0	0.0034	72.5
II	4	25	0.1851	2.0	0.0067	64.3
	5	25	0.1885	5.0	0.017	56.3
III	6	22	0.2089	0	0	96.6
	7	22	0.2002	0.5	0.0017	64.3
	8	22	0.1949	1.0	0.0034	51.8
	9	22	0.2081	5.0	0.017	28.6
IV	10	21	0.2080	5.0	0.017	29 0
	11	21	0.2075	10.0	0 034	22.0
	12	21	0.2010	20.0	0.067	18.7

The results of experiments are shown in Table 1. The amount of oxygen dissolved in the carbon tetrachloride solution was calculated on the same basis as described in the previous paper.[1] The relation between the amount of oxygen and the extent of addition is illustrated in the accompanying figure, the upper curve representing the experiments at 25–26° (Exp. 1, 2, 4, and 5) and the lower those at 21–22° (Exp. 6–12). The addition in vacuum proceeded so rapidly that the extent in 22 hours was nigh upon 100% both at 21–22° and at 25–26°, while in the presence

of oxygen a difference of about 4° in the temperature caused a remarkable separation of the two curves.



Millimol of Oxygen in 30 c.c. CCl_4 Solution containing 1 millimol of Cinnamic Acid.

II. **The Effect of Peroxides.** Benzoyl peroxide was used. The commercial product was dried in vacuum over sulphuric acid. The purity was found 99.63% by iodometry in acetone solution.[3] Weighed amounts of benzoyl peroxide were dissolved together with cinnamic acid in carbon tetrachloride in the reaction tubes, the experimental procedure in all other respects being the same as described above.

In the iodometric determination of the extent of addition the added peroxide might liberate iodine, thus causing too small values of the extent. However, it was found that benzoyl peroxide liberates only a trace of

(3) H. Gelissen and P. H. Hermans, *Ber.*, **59** (1926), 68.

iodine under the conditions as described above: 0.05 g. of benzoyl peroxide was dissolved in 30 c.c. of carbon tetrachloride, and the solution was mixed with 30 c.c. of concentrated aqueous potassium iodide. The mixture, after placed in the dark during such a time (6–7 minutes) as required usually in the iodometric determination of the extent of reaction, was titrated with N/10 sodium thiosulphate. Only 0.05 c.c. was consumed, while 0.05 g. of the peroxide corresponds theoretically to about 4 c.c. of N/10 sodium thiosulphate. The amounts of the peroxide used in the additions ranged from about 0.1 to 0.01 g., and the volumes of N/10 sodium thiosulphate required to titrate the iodine liberated by bromine remaining after the reactions in the presence of the peroxide from 3.7 to 16 c.c. The correction value −0.05 c.c. for 0.05 g. of the peroxide was taken into account in all titrations in the presence of the peroxide under the assumption that the peroxide had not been decomposed during the reaction. Although the peroxide seems to be subject to a chemical change with bromine as indicated by the experiments described below, this assumption is valid so long as the peroxidic oxygen remains unchanged.

Benzoyl peroxide is not decomposed by cinnamic acid in carbon tetrachloride, or strictly speaking, the amount of peroxidic oxygen is not changed. Benzoyl peroxide (0.1084 and 0.0108 g. corresponding to 0.1132 and 0.0113 g. of iodine respectively) and cinnamic acid (0.1481 g. each) were dissolved in carbon tetrachloride (30 c.c. each), and the solution was sealed in vacuum in a tube in the same manner as in the experiments of addition. After 22 hours (in the dark at room temperature) the amount of the peroxide was determined by iodometry in acetone solution and found to be unchanged (0.1166 and 0.0117 g. of iodine respectively).

On the other hand, benzoyl peroxide seems to react with bromine in carbon tetrachloride. Just in the same manner as in the experiments of addition, benzoyl peroxide and bromine was dissolved in carbon tetrachloride in absence of air. After 22 hours' standing in the dark at room temperature, the solution was mixed with aqueous potassium iodide, bromine being replaced by iodine, and then, by adding acetone, the peroxide was converted into iodine. The total iodine thus liberated was determined and compared with the value calculated from the initial amounts of benzoyl peroxide (the purity 99.63% being taken into account) and bromine. In Table 2 the change is shown in terms of the corresponding amounts of bromine (designated as g.Br).

The values of decrease shown in Table 2 are less than, and roughly half, the amounts (expressed in g.Br) of benzoyl peroxide used. If this decrease had been caused by the decomposition of the peroxide, matters

Table 2.

Benzoyl peroxide (g.)	Benzoyl peroxide (g.Br)	Bromine (g.)	Total (g.Br)	Found after reaction (g.Br)	Decrease (g.Br)
0.1084	0.0714	0.2106	0.2820	0.2517	0.0303
0.1084	0.0714	0.1852	0.2566	0.2079	0.0487
0.2168	0.1427	0.1813	0.3240	0.2367	0.0873

would have been simpler, because the decrease in the amounts of the peroxide would have been no obstacle to qualitative consideration of the results of additions in the presence of the peroxide, and, even if oxygen should have been liberated by the decomposition, its retarding effect on the addition having been well explored, little difficulty would have been encountered in learning the effect of the peroxide from the results of experiments. However, it had to be assumed that a part of bromine was consumed by the peroxide, and that a substitution took place.[4] If so, while the amount of the peroxidic oxygen remains unchanged, bromine will be consumed both by cinnamic acid and by benzoyl peroxide in the reaction of bromine with cinnamic acid in the presence of the peroxide. What might complicate matters more seriously is the formation of hydrogen bromide by the substitution. On this account, it had to be determined what influence is exerted by hydrogen bromide on the addition of bromine to cinnamic acid.

Fortunately enough, it has been found that hydrogen bromide is indifferent to the addition reaction either in presence or in absence of oxygen: As shown in Table 3, in the presence of hydrogen bromide the addition proceeded as rapidly as in vacuum and cinnamic acid dibromide melting at 198° separated in quantity (Exp. 13), while hydrogen bromide exerted no accelerating effect on the reactions retarded by the addition of oxygen (Exp. 15–17).

Now the authors are ready for discussing the results of additions in the presence of benzoyl peroxide, which are summarized in Table 4. The apparent extent of addition corresponds to the total amount of bromine consumed. If the apparent extent is corrected under the assumption that the peroxide consumed half its number of molecules of bromine, the values given in the last column of Table 4 are obtained. However,

(4) Compare L. Vanino and E. Uhlfelder, *Ber.*, **33** (1900), 1046.

Table 3.

Group of exp.	No. of exp.	Temp. (°C.)	Bromine (g.)	Oxygen admitted (c c., n.p.t.)	Hydrogen bromide admitted (c.c., n.p.t.)	Extent of addition (%)
V	13	17	0.2043	0	2.4	96.9
VI	14	17	0.1910	5.0	0	14.7
	15	17	0.1943	5.0	2.0	19.3
VII	16	17	0.2144	5.0	2.0	11.6
	17	17	0.2167	5.0	1.0	15.2

Table 4.

Group of exp.	No. of exp.	Temp. (°C.)	Bromine (g.)	Benzoyl peroxide		Extent of addition	
				(g.)	(millimol)	Apparent (%)	Corrected (%)
I	1	26	0.1820	0	0	96.9	96.9
	3	26	0.1850	0.0108	0.045	96.7	94
VIII	19	25	0.1976	0.0217	0.090	95.2	91
	20	25	0.1923	0.0434	0.179	97.2	88
	21	25	0.1919	0.1084	0.448	99.2	77

they do not indicate any retarding effect of the peroxide, because the amount of bromine used was only slightly excessive to cinnamic acid alone, and nearly all of it was consumed. On the contrary, the fact that the more benzoyl peroxide was present the sooner the crystals of cinnamic acid dibromide (melting point 198°) appeared indicates qualitatively the accelerating effect of benzoyl peroxide, provided that the presence of the peroxide or the products from the reaction of the peroxide with bromine did not diminish the solubility of the dibromide.

The accelerating effect of benzoyl peroxide is definitely demonstrated by the additions in the presence of both oxygen and the peroxide. The results collected in Table 5 show the effect of the peroxide on the reactions retarded by admitting 5 c.c. of oxygen.

The apparent extent of addition was corrected on the basis of the same assumption as stated above (the last column of Table 5). It can

Table 5.

Group of exp.	No. of exp.	Temp. (°C.)	Bromine (g.)	Benzoyl peroxide		Oxygen		Extent of addition	
				(g.)	(m.mol)	Admitted (c.c., n.p.t.)	Dissolved in CCl_4 sol. (m.mol)	Apparent (%)	Corrected (%)
VII	18	17	0.2164	0.0217	0.090	5.0	0.017	56.9	52
IX	22	19	0.1990	0.0217	0.090	0	0	97.2	93
	23	19	0.1966	0	0	5.0	0.017	20.8	20.8
	24	19	0.1952	0.0217	0.090	5.0	0.017	77.5	73
X	25	20	0.2107	0	0	5.0	0.017	20.1	20.1
	26	20	0.2106	0.0108	0.045	5.0	0.017	49.9	48

be seen from the table that the presence of the peroxide compensated partly the retardation by oxygen. As it can be assumed that there should be no direct interference between the peroxide and oxygen, the effect of the former on the reactions retarded by the latter must be attributed to the inherent accelerating effect of the benzoyl peroxide on the addition of bromine to cinnamic acid.

Although it has been proved that hydrogen bromide is quite indifferent to the reaction, it does not necessarily exclude the possibility that it might be active in cooperation with a peroxide. But this seems improbable from the fact that hydrogen bromide is inactive in the addition of bromine to cinnamic acid even in the presence of oxygen while it is active in the isomerization of isostilbene into stilbene in the presence of either benzoyl peroxide or oxygen.[5]

Some contradictions may be found between the results recorded in the present paper and those published by P. W. Robertson and coworkers.[6] But, no mention being made of air and light there, no comparison can be justified. In this connection, however, it may be emphasized that the addition of bromine to cinnamic acid in carbon tetrachloride under the conditions of the experiments carried out by the present authors is homogeneous[1] and the addition product was always cinnamic acid dibromide melting at 198°.

(5) See the following paper, this volume, p. 507.

(6) P. W. Robertson, N. T. Clare, K. J. McNaught, and G. W. Paul, *J. Chem. Soc.*, **1937**, 335.

Addendum: The Addition in the Presence of Reduced Iron. The perfect resistance of iron and nickel against hydrogen bromide was essential to the success in the experiments on the addition of hydrogen bromide to allyl bromide in the presence of these metals. If they were resistant also to bromine in carbon tetrachloride, interesting results might be expected from the experiments on the addition of bromine to cinnamic acid in the presence of these metals. However, it has been found that these metals are subject to serious attack by bromine in carbon tetrachloride, and in an addition in the presence of reduced iron the consumption of bromine was more than 100% in reference to cinnamic acid.

Summary.

(1) The relation between the extent of addition of bromine to cinnamic acid in carbon tetrachloride and the amount of oxygen present has been shown.

(2) It has been indicated that hydrogen bromide is indifferent to the reaction of bromine with cinnamic acid in carbon tetrachloride either in presence or in absence of oxygen.

(3) The accelerating effect of benzoyl peroxide on the addition of bromine to cinnamic acid in carbon tetrachloride has been demonstrated.

(4) In all cases, namely in vacuum and in the presence of any of oxygen, benzoyl peroxide, and hydrogen bromide, the products separating out in crystals were cinnamic acid dibromide melting at 198°.

(5) All the results mentioned above were obtained from the additions in the dark at room temperature.

The authors express their sincere thanks to the Nippon Gakujutsu Shinko-kwai (the Japan Society for the Promotion of Scientific Research) for a grant.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

The Effect of Oxygen and Reduced Nickel on the Catalytic Action of Hydrogen Bromide in the Isomerization of Isostilbene into Stilbene.

By Yoshiyuki URUSHIBARA and Osamu SIMAMURA.

(Received November 2nd, 1937.)

The influence of oxygen and ferromagnetic metals on the addition of hydrogen bromide or bromine to ethylenic compounds has been investigated in this laboratory.[1] The scope of investigation has been extended to other types of reactions and it has been examined whether or not the cis-trans-isomerization is influenced by the presence of oxygen and ferromagnetic metals. Nevertheless neither oxygen nor reduced nickel showed a defined accelerating effect on the isomerization of dimethyl maleate into dimethyl fumarate and of isostilbene into stilbene even in the heat (in absence of solvents).[2]

Then the authors became aware of a short communication by M. S. Kharasch, J. V. Mansfield, and F. R. Mayo.[3] They found that in the dark carefully purified isostilbene, dissolved in benzene, was not isomerized into stilbene by hydrogen bromide when the reactants were mixed either in air or in vaccum, or in the presence of antioxidants, and that the addition of a peroxide to the reaction mixture caused complete isomerization in a few minutes.

The present authors' experiments in absence of solvents resulted in part similarly to the experiments in benzene solution by the American investigators: The presence of hydrogen bromide alone did not accelerate the isomerization of isostilbene into stilbene in the dark at room temperature, but the addition of a sufficient amount of benzoyl peroxide caused complete solidification of isostilbene into stilbene in a few minutes.

Oxygen showed a similar effect on the same reaction: When dry oxygen and dry hydrogen bromide were introduced into the tube con-

(1) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754, 798; **12** (1937), 51, 138, 173, 356, 499.

(2) B. Tamamushi and H. Akiyama observe that the isomerizations of dimethyl maleate into dimethyl fumarate and of maleic acid into fumaric acid in aqueous solution are accelerated by the presence of molecular oxygen. *Z. Elektrochem.*, **43** (1937), 156; this Bulletin, **12** (1937), 382.

(3) *J. Am. Chem. Soc.*, **59** (1937), 1155.

taining isostilbene, the latter solidified completely in a few minutes in the dark at room temperature. The American investigators state that isostilbene in benzene solution was not isomerized to stilbene by hydrogen bromide even when the reactants were mixed in air. It may be suspected that no sufficient amount of oxygen was absorbed under the conditions of their experiments or the solvent prevented oxygen from exerting its influence.

As it was found that isostilbene does not form any peroxide with oxygen in the dark and even in diffuse light, the effect of oxygen must be attributed to the action of molecular oxygen. On the other hand, from the experimental evidence so far obtained, it cannot be decided whether benzoyl peroxide is active as such or oxygen liberated by its decomposition is the real agent.

Reduced nickel, which exhibits a catalytic action similar to that of oxygen in the addition of hydrogen bromide to allyl bromide,[4] was found also to cooperate with hydrogen bromide to accelerate the isomerization of isostilbene into stilbene. However, the effect displayed by reduced nickel and hydrogen bromide was much smaller than that by oxygen and hydrogen bromide so far as the preliminary experiments indicated. Reduced nickel contained in a reaction tube was heated at 310–320° in the atmosphere of hydrogen and then in vacuum, and cooled in vacuum. The tube, after introducing hydrogen bromide, was sealed, and isostilbene contained in a side tube attached to the reaction tube was decanted on the reduced nickel. The crystals of stilbene began to appear in the course of ½–3 hours in the dark at room temperature, and finally the whole mass solidified. The change was naturally much more rapid at the temperature of the hot water bath.

Thus it has been shown that oxygen and reduced nickel exert no direct influence on the isomerization of isostilbene into stilbene, but cooperate with hydrogen bromide, which is also inactive by itself, in accelerating the isomerization. It seems very probable that in the presence of oxygen or reduced nickel hydrogen bromide is excited to an active catalyst to promote the isomerization.

In a theory advanced for explaining the influence of oxygen and ferromagnetic metals on the addition of hydrogen bromide to allyl bromide, one of the authors (Y. U.) with M. Takebayashi assumed that these active catalysts exert some physical influence on allyl bromide,[5] but they reserved the possibility that the substance which is influenced by

(4) This Bulletin, **11** (1936), 692, 754; **12** (1937), 51.
(5) This Bulletin, **12** (1937), 54, 175.

oxygen and ferromagnetic metals might be hydrogen bromide.[6] The results recorded in the present paper suggest the possibility that hydrogen bromide is excited by oxygen or ferromagnetic metals and the excited hydrogen bromide adds rapidly to allyl bromide to give the abnormal addition product.

M. S. Kharasch and co-workers in the cited communication bring forward a hypothesis that bromine atoms are the active catalysts in the isomerization of isostilbene into stilbene, and seem to be of the opinion that bromine atoms are responsible also for the so-called peroxide effect in the addition of hydrogen bromide to unsaturated compounds.[7] However, the effect of ferromagnetic metals on the addition of hydrogen bromide to allyl bromide cannot be explained by assuming bromine atoms, because the action of ferromagnetic metals, in contrast with oxygen and peroxides, does not undergo even the slightest modification in the presence of an antioxidant.[8] Moreover, it may be difficult to introduce a similar idea into the case of the addition of bromine to cinnamic acid in carbon tetrachloride, where oxygen retards the rate of addition while peroxides accelerate the reaction and hydrogen bromide is indifferent either in presence or in absence of oxygen.[9]

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Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

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(6) This Bulletin, **12** (1937), 176.

(7) They state the hypothesis is proposed in an article in press, but the article is not yet available here.

(8) This Bulletin, **11** (1936), 754.

(9) This Bulletin, **12** (1937), 356, 499.